

FLAMMABILITY LIMITS OF SATURATED VAPORS: TOLUENE-OXYGEN-CARBON DIOXIDE MIXTURES

SILVESTRO CRESCITELLI, SALVATORE MELI, GENNARO RUSSO and VINCENZO TUFANO

Istituto di Chimica Industriale ed Impianti Chimici, Università di Napoli, 80125 Napoli (Italy)

(Received October 22, 1979; accepted in revised form January 2, 1980)

Summary

The flammability limits of saturated toluene-oxygen-carbon dioxide mixtures have been evaluated using a new experimental technique, the experiments being carried out in a closed stainless steel vessel in which both saturated gaseous and liquid phases are present. The flammability zone was determined in the range 40–120°C and 1–15 atm. at different oxygen/carbon dioxide ratios by direct measurement, that is without the extrapolation procedure necessary when using the classic techniques.

The good agreement obtained with the data available in the literature shows the effectiveness of this new technique, which proves also to be simpler, cheaper and safer than the classic one.

Introduction

The liquid phase oxidation of toluene with air using cobalt salts as catalyst is one of the routes to benzoic acid [1, 2]; since benzoic acid is a widely used chemical intermediate, whose major utilization is the SNIA caprolactam process, it is of great relevance to obtain any improvement in its production.

In some similar processes, such as ethylene oxidation to ethylene oxide, or cumene oxidation to cumene hydroperoxide, a more economic production may be in some cases obtained using oxygen as oxidant instead of air [3]. Therefore, it seems worthwhile to evaluate the feasibility of an oxygen-based process for toluene oxidation to benzoic acid.

Of the technical factors to be taken into account when evaluating this alternative process, an important factor is the safety measures to be taken against accidental explosions which may occur in the gaseous mixtures present in the head of the reactor, in the cooling equipment and in the recycle lines. When substituting oxygen for air, carbon dioxide may be used as diluent instead of nitrogen. In fact, not only is carbon dioxide available in situ as a reaction by-product, but it is also more effective in narrowing the flammability zone.

Fig. 1 shows a schematic diagram of the experimental apparatus. All the pressurized equipment is placed inside a blast cubicle, while the control and

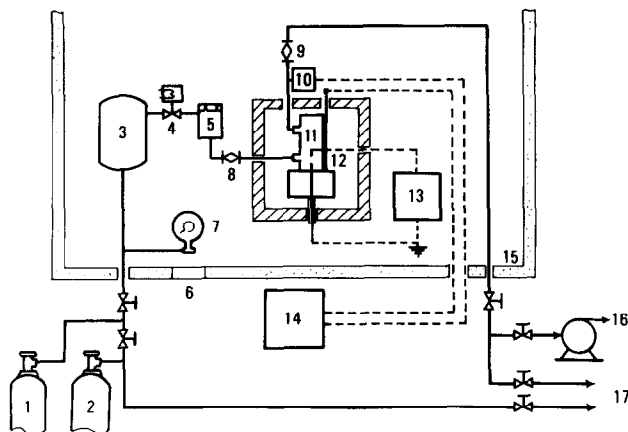


Fig. 1. Experimental apparatus. 1, O₂-CO₂ mixture cylinder; 2, N₂ cylinder; 3, O₂-CO₂ reservoir; 4, solenoid valve; 5, toluene reservoir; 6, window; 7, manometer; 8 and 9, ball valves; 10, pressure transducer; 11, explosion vessel; 12, thermocouple; 13, ignition device; 14, chart recorder; 15, safety wall; 16, vacuum pump; 17, vent.

the measurement devices are in the adjacent laboratory. The test vessel is a stainless steel cylinder, 45 mm i.d. and 145 mm long, located in an electrically heated oven in which hot air circulation gives uniform temperatures as measured by thermocouples.

The experimental technique used has been widely discussed [5].

Using this procedure, it was possible to obtain a fast heating and vaporization of toluene and a good mixing in the gaseous phase. This was verified in some initial runs in which the temperature and the pressure were measured during the filling procedure with and without toluene. The mixture may be quickly ignited with a residence time of approx. 20 s under the test conditions, avoiding the preoxidation reactions that may interfere with a correct measurement of the flammability limits, as discussed in a previous paper [6].

A spark plug at the bottom of the explosion vessel is used, so that the more conservative upward limits are determined. Sparks of 0.1 J can be produced between two tungsten electrodes, whose tips are 2 mm apart, by an inductive-capacitive power supply which gives voltages up to 30 kV.

A Disa pressure measurement system (51 E01 reactance converter, 51 E02 oscillator and 51 E10 transducer), coupled with an Hewlett-Packard chart recorder, was used to measure the maximum and the residual pressures following ignition in order to provide information regarding the reactivity of the mixture tested.

Therefore, as a first step in evaluating the feasibility of the oxygen process, it is necessary to know the flammability limits of the ternary system toluene-oxygen-carbon dioxide. While the system toluene-air-nitrogen has been extensively studied [4], no data are available for toluene-oxygen-carbon dioxide mixtures. When planning the experimental runs, one must take

into account that the gaseous mixtures present in the plant in all cases contain toluene as saturated vapor, while different oxygen/carbon dioxide ratios may be postulated, depending on the operating conditions of the different equipment of the plant. Hence, experiments must be carried out to determine the flammability limits of saturated toluene-oxygen-carbon dioxide mixtures at different temperatures, pressures and oxygen/carbon dioxide ratio, to evaluate the range of operative conditions in which the plant may safely operate.

Experimental technique

In similar cases, the usual experimental technique has been used to measure the flammability limits of non-saturated mixtures; then the data for saturated mixtures have been obtained by extrapolation, and this may generate incorrect results.

To measure directly the flammability limits of saturated vapors, a new experimental technique has been developed, which allows the carrying out of experimental runs in a closed vessel in which both gaseous and liquid phases are present. This condition is obtained by feeding a pre-determined amount of toluene into the explosion vessel together with a suitable amount of pressurized oxygen-carbon dioxide mixture.

The experimental technique was used to measure, starting from a non-flammable mixture, the limit pressure necessary to support the propagation of a flame at constant temperature and oxygen-carbon dioxide ratio. When operating close to the rich limit, the initial pressures of the following tests were increased, so as to increase the oxygen/toluene ratio, until a flammable mixture was found. However when operating close to the weak limit, the initial pressures were progressively lowered, to decrease the oxygen/toluene ratio.

A large amount of soot is produced during flame propagation in rich mixtures; it was therefore necessary to clean up the test vessel after each run carried out with a flammable rich mixture, to obtain reproducible results in the following tests.

The measurements of the weak flammability limits may be affected by the combustible fog possibly present in the vessel: nevertheless this effect may be minimized using a suitable amount of toluene.

Results and discussion

The flammability limits of the saturated toluene-oxygen-carbon dioxide system were measured using the above-mentioned technique in the range 40–120°C and 1–15 atm. at different oxygen/carbon dioxide ratios.

In Fig. 2 the experimental results obtained at $T = 120^\circ\text{C}$ are reported. The oxygen/(oxygen + carbon dioxide) percentage, Y , is plotted as a function of the initial pressure. The border line between flammable (above the line) and

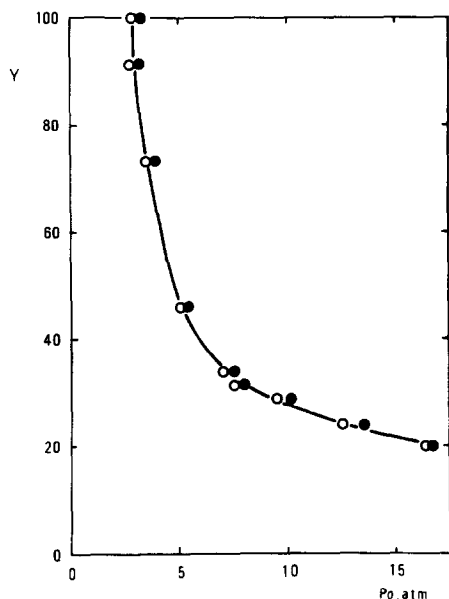


Fig. 2. Oxygen/(oxygen + carbon dioxide) ratio at the flammability limit Y , versus initial pressure, P_0 , at $T = 120^\circ\text{C}$. \circ , non-flammable mixtures; \bullet , flammable mixtures.

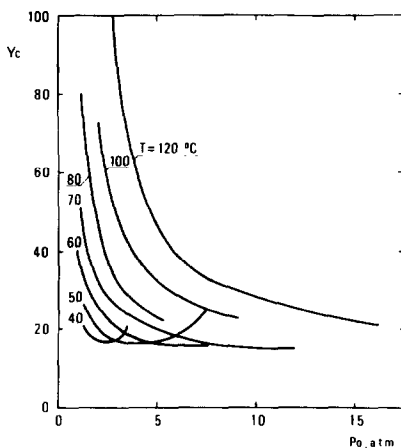


Fig. 3. Corrected values of the oxygen/(oxygen + carbon dioxide) ratio, Y_c , versus the initial pressure, P_0 , for different temperatures.

non-flammable mixtures is evaluated with an accuracy of about 0.3 atm., due to the experimental technique used. The values of Y plotted here are the oxygen percentages in the gas loaded in the reservoir 3, as evaluated by a paramagnetic oxygen analyzer (Taylor Servomex OA 137), whose accuracy is very high (about 0.1%). These percentages would also be the values obtained in the test vessel if no solubility in the liquid phase and ideal gas behaviour could be assumed. However, the solubility of carbon dioxide and oxygen in the liquid phase present in the explosion vessel and the non-ideal behavior of the gaseous phase do affect the gas composition in the explosion vessel. Therefore, the actual composition obtained in the test vessel has been calculated taking into account the two above-mentioned effects, using the data available in the literature [7, 8]. The difference between the calculated and the measured composition values is not high: for instance, the maximum correction for Y , i.e. the one at the lowest temperature and the lowest oxygen content, is about 2.5% of its value. However, all the data presented in the following have been corrected using this criterion. In Fig. 3 the results obtained at different temperatures are plotted as a function of the initial pressure. For the highest temperatures the actual values Y_c of the oxygen/(oxygen + carbon dioxide) ratio in the vapour phase sharply decrease on increasing the pressure: for temperatures lower than 70°C a flat minimum is observed. This minimum marks the transition between the rich flammabil-

ity limit (the left side of the curve, i.e. the one at the lowest pressures) and the weak flammability limit. At the highest temperatures the weak limit has not been reached in the range of pressures examined. The oxygen percentage corresponding to the minima of the curves is the limiting oxygen content that makes a mixture unable to propagate a flame for any pressure at a fixed temperature. This value slightly decreases on increasing the temperature, from 17.0% at $T = 40^\circ\text{C}$ to 15.2% at $T = 70^\circ\text{C}$.

It is well known that the actual flammability limits are somewhat uncertain, because they depend on the experimental technique used [6]. An indirect measurement of this uncertainty is given in Fig. 4 in which the maximum measured explosion pressures are plotted as a function of the initial pressure for $T = 50^\circ\text{C}$ and $Y_c = 24.0\%$. It may be observed that the pressure increase attains a maximum well inside the flammability zone, while close to the flammability limits only very small pressure increases are measured, showing a very low reactivity of the mixtures tested. Therefore, with different experimental apparatus, small differences in the flammability limits may be observed.

Fig. 5 shows a plot of the equivalent ratio $\Phi = (C_7H_8/O_2)/(C_7H_8/O_2)_{\text{stoich}}$ at the flammability limits versus the initial pressure, for the different temperatures examined. For any fixed temperature, the equivalence ratio at the flammability limit decreases on increasing the pressure, moving from the rich limit towards the weak one. For the lowest temperatures, comparison between Figs. 3 and 5 shows that the minimum points occur in the range $1.2 < \Phi < 1.8$. This is in good agreement with the general finding that the

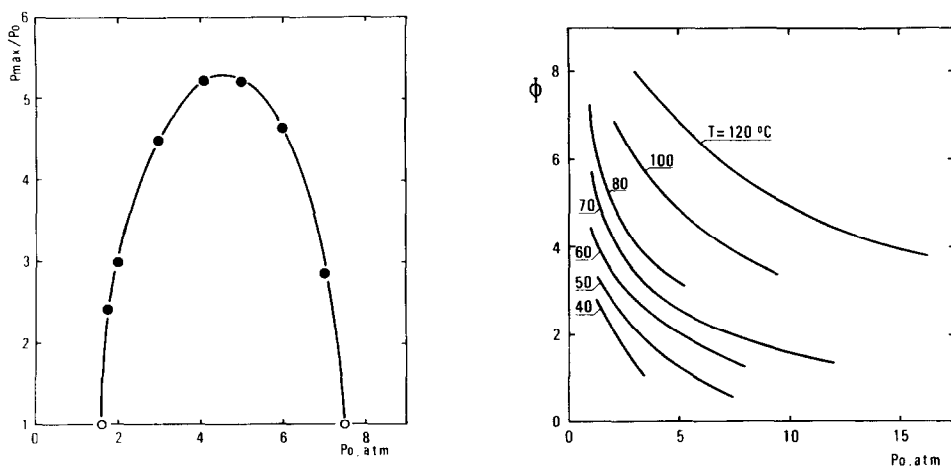


Fig. 4. Nondimensional maximum explosion pressure versus the initial pressure, P_0 , for $T = 50^\circ\text{C}$ and $Y_c = 24\%$.

Fig. 5. Equivalence ratio, $\Phi = (C_7H_8/O_2)/(C_7H_8/O_2)_{\text{stoich}}$ at the flammability limit versus the initial pressure, P_0 , at different temperatures.

more reactive mixtures at any fixed diluent content occur at an equivalence ratio slightly greater than one.

In Fig. 6 the flammability zones for different temperatures are reported as a function of the diluent percentage and of the equivalence ratio. It is worthwhile stressing that the pressure varies along each isothermal line. The figure shows that the flammability limits widen on increasing the temperature and the pressure: on the other hand, the limit diluent percentage to avoid flame propagation varies only slightly, from about 80.5% at $T = 40^\circ\text{C}$ to about 82% at $T = 70^\circ\text{C}$, in a similar way to the oxygen limit percentage plotted in Fig. 3.

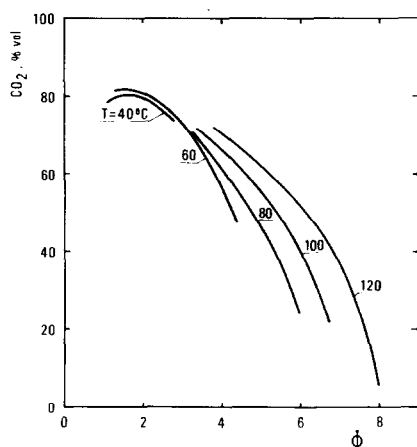


Fig. 6. Carbon dioxide percentage at the flammability limit versus equivalence ratio ϕ at different temperatures.

TABLE 1

Limit pressures at 21% oxygen

T ($^\circ\text{C}$)	Limit pressure (atm.)	
	Diluent N_2	Diluent CO_2
50	1.0	1.9
60	2.0	2.9
70	3.1	4.6
80	4.3	6.5
85	5.0	7.7
90	5.6	8.9
100	7.0	11.5
110	8.3	13.8
120	9.5	16.3
125	10.0	

The results obtained may be compared with those of Yantovskii et al. [4], which refer to the toluene-air-nitrogen system. The limit pressures at different temperatures for a fixed oxygen percentage ($Y_c = 21\%$), obtained by interpolating the two sets of experimental data, are presented in Table 1. It may be observed that the limit pressures obtained when using carbon dioxide as diluent are slightly higher than those obtained when using nitrogen, but show the same trend as a function of temperature. In conclusion, taking into account the higher extinction power of carbon dioxide as compared with nitrogen, the agreement between the two sets of data is fairly good.

Conclusions

A new experimental technique for measuring the flammability limits of gaseous mixtures containing saturated vapors has been set up and used for the toluene-oxygen-carbon dioxide system. This technique allows one to rapidly prepare in the experimental vessel the saturated mixtures to be tested and, unlike the classic method, to obtain directly the desired results without extrapolating the experimental data obtained with non-saturated mixtures.

Moreover, this technique appears less expensive with regard to the amount of reactants necessary for each run and, more importantly, also appears safer, because the reactive mixtures are present only in the explosion vessel.

In conclusion, it seems very promising for obtaining similar data for other saturated hydrocarbon-oxygen-diluent systems, which are data not available in the literature in spite of their practical relevance.

Acknowledgements

This work has been supported by the Fondazione Oronzio De Nora, Milan, and Laboratorio di Ricerche sulla Combustione, CNR, Naples. The help of Dr. L. Pistone in many steps of the experimental work is greatly appreciated.

References

- 1 I. Donati, G. Sioli and M. Taverna, *Caprolattame da toluene: il processo SNIA Viscosa*, *Chim. Ind.*, 50 (1968) 997.
- 2 R. Mattone, G. Sioli and L. Giuffrè, *Caprolactam without ammonium sulfate*, *Hydrocarbon Process.*, January (1975) 83.
- 3 *Air vs. oxygen*, *Hydrocarbon Process.*, March (1976) 69.
- 4 S.A. Yantovskii, I.Yu. Sidorina and M.V. Chernyak, *Conditions of safe oxidation of toluene by atmospheric oxygen*, *Int. Chem. Eng.*, 7 (1967) 144.
- 5 S. Giannetta, *Thesis in Industrial Chemistry*, Istituto di Chimica Industriale ed Impianti Chimici dell'Università di Napoli, 1979.
- 6 S. Crescitelli, G. Russo and V. Tufano, *The influence of different diluents on the flammability limits of ethylene at high temperatures and pressures*, *Proc. "Colloque sur la Sécurité dans l'Industrie Chimique"*, Mulhouse, 1978, p. 37; *J. Hazardous Materials*, 3 (1979) 167.
- 7 Landolt-Börnstein, *Zahlenwerte und funktionen*, Vol. IV, part 4, Springer, Berlin, 1976.
- 8 O.A. Hougen, K.M. Watson and R.R. Ragatz, *Chemical Process Principles*, Vol. II, John Wiley, New York, 1966.